

Organosilicon Compounds XV. Cleavage of the Silicon-Carbon Bond of 2-Trimethylsilyl-1-methylimidazole and 2-Trimethylsilyl-1-methylbenzimidazole.

Frank H. Pinkerton and Shelby F. Thames (1)

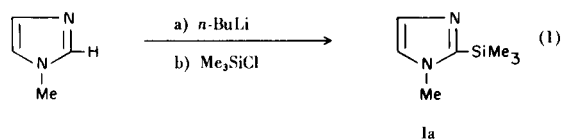
Department of Polymer Science, University of Southern Mississippi,  
Hattiesburg, Mississippi 39401

Received July 29, 1971

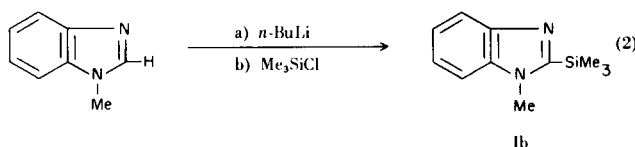
Cleavage of the aryl-silicon bond of 2-trimethylsilyl-1-methylimidazole (Ia) and 2-trimethylsilyl-1-methylbenzimidazole (Ib) has been effected by five carbonyl reagents, *i.e.* aldehydes, acid halides, chloroformates, anhydrides and isocyanates, to provide a novel synthetic route to a host of functionally substituted heterocycles. Compound Ia reacted exothermically at room temperature with four of the five carbonyl reagents.

The labile nature of aryl-silicon bonds toward both acids and bases has been documented in organosilicon chemistry for many years. However, the systematic investigation of the cleavage of aryl-silicon bonds by neutral reagents has been initiated only recently. In this regard, Anderson, Webster, *et al.* (2), have shown the pyridyl-silicon bond of 2-trimethylsilylpyridine to be susceptible to cleavage by alcohols and water to form unsubstituted pyridine. More recently, investigations at this laboratory have shown that the aryl-silicon bond of 2-trimethylsilylpyridine (3,4) and 2-trimethylsilylbenzothiazole (5) is readily cleaved by several carbonyl reagents, *i.e.* aldehydes, acid halides, chloroformates and anhydrides. In the present study, this aryl-silicon cleavage reaction by carbonyl reagents has been extended to two additional silylheterocycles, 2-trimethylsilyl-1-methylimidazole (Ia) and 2-trimethylsilyl-1-methylbenzimidazole (Ib).

As part of our general investigation of the cleavage of aryl-silicon bonds by neutral carbonyl reagents, we have sought to extend this reaction to include a variety of silylheterocyclic systems. In this regard, Shirley and Alley have previously documented that 1-methylimidazole (6) and 1-methylbenzimidazole (7) can be successfully metalated with *n*-butyllithium. By utilizing their low temperature metalation procedure described for 1-methylimidazole, followed by condensation with trimethylchlorosilane, we have subsequently prepared (Ia) in 20-30% yield [eqn. (1)]. Likewise, 1-methylbenzimidazole was metalated

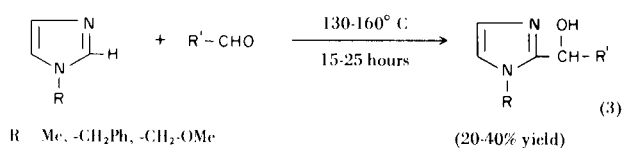


with *n*-butyllithium at  $-75^\circ$ , and the resultant organolithium derivative was condensed with trimethylchlorosilane at  $-75^\circ$  with gradual warming to room temperature to afford (Ib) in 70-80% yield [eqn. (2)]. Neither Ia nor Ib had been reported previously in the literature.



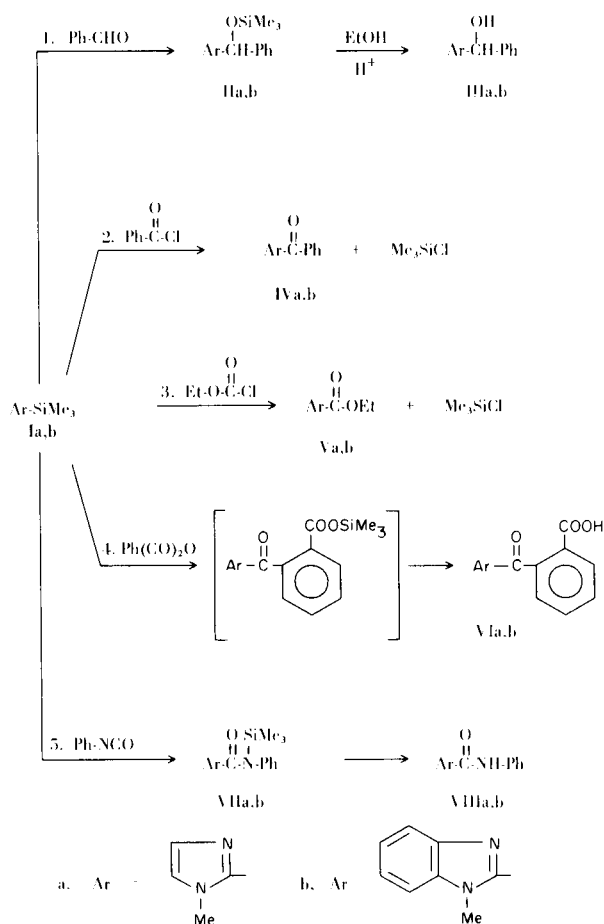
The aryl-silicon bond of Ia proved to be extremely reactive toward various carbonyl reagents. For example, the reaction of Ia with benzaldehyde, benzoyl chloride, ethyl chloroformate and phenyl isocyanate proceeded exothermically, when the carbonyl reagent was added dropwise to the silane, to afford a 91% yield of phenyl-2-(1-methyl)imidazolylmethyl trimethylsilyl ether (IIa), an 84% yield of phenyl 2-(1-methyl)imidazolyl ketone (IVa), an 89% yield of ethyl 2-(1-methyl)imidazolecarboxylate (Va), and a 95% yield of *N*-trimethylsilyl-*N*-phenyl-2-(1-methyl)imidazolecarboxamide (VIIa), respectively (Scheme 1). Phthalic anhydride did not appear to react with Ia upon mixing at room temperature; however, an exothermic reaction was observed after heating the reaction mixture to  $40\text{-}50^\circ$  to afford, after exposure of the product to the atmosphere, an 86% yield of 2-carboxyphenyl 2-(1-methyl)imidazolyl ketone (VIa). It appeared that the silyl ester was formed initially in this reaction, and as a result of the labile nature of the Si-O bond, was cleaved by moisture to VIa, although isolation of this intermediate product was not attempted.

That Ia was reactive with benzaldehyde is not unexpected in light of the reported thermal condensation of



1-methylimidazole with various aldehydes (8) [eqn. (3)]. This reaction was initially discovered utilizing formaldehyde and chloral in the early 1900's but only recently has it been extended to include benzaldehyde, *n*-heptaldehyde and other aldehydes. Furthermore, two observations in the present investigation reflect the enhanced polarity of the C-Si bond of Ia as compared to the C-H bond of 1-methylimidazole. First, in contrast to the severe conditions employed in the reactions of 1-methyl-

SCHEME 1



imidazole, Ia reacted exothermically at room temperature when benzaldehyde was added dropwise. In addition, the reaction of Ia with benzaldehyde affords a 91% yield of the silyl ether (IIa), while the reaction of 1-methyl-

imidazole with aldehydes characteristically provided low yields of the corresponding carbinols.

As was the case with the aryl-silicon bond of 2-trimethylsilylbenzothiazole (5), the silicon-carbon bond of Ib also proved to be unusually labile toward neutral carbonyl reagents. For example, Ib was reacted with benzaldehyde at 180° for 16 hours to afford an 86% yield of phenyl-2-(1-methyl)benzimidazolylmethyl trimethylsilyl ether (IIb). In addition, Ib reacted with benzoyl chloride, ethyl chloroformate, phthalic anhydride and phenyl isocyanate to afford an 80% yield of phenyl 2-(1-methyl)benzimidazolyl ketone (IVb), a 72% yield of ethyl 2-(1-methyl)benzimidazolecarboxylate (Vb), a 71% yield of 2-carboxyphenyl 2-(1-methyl)benzimidazolyl ketone (VIb) and an 88% yield of *N*-trimethylsilyl-*N*-phenyl-2-(1-methyl)benzimidazolecarboxamide (VIIIb), respectively (Scheme 1). Again, the reaction of Ib with phthalic anhydride was thought to proceed through the intermediate silyl ester, even though no attempt was made to isolate this specie. The silyl ethers (IIa, b) and *N*-silylamides (VIIa, b) produced herein were readily converted to the corresponding alcohols and amides by refluxing with 95% ethanol.

Previously, we have described (4) the dependence of these cleavage reactions on the polar nature of both the aryl-silicon bond and the carbonyl cleavage reagent. Indeed, the present investigation verifies the importance of the polarity of the aryl-silicon bond on the apparent ease of cleavage. For example, we have recently documented (9) the sluggish reactivity of 2-trimethylsilyl-1-methylpyrrole with benzoyl chloride and phenyl chloroformate and the non-reactivity of this silylheterocycle with benzaldehyde and ethyl chloroformate. In contrast, Ia and Ib reacted efficiently with these same reagents to provide excellent yields of a variety of interesting heterocyclic derivatives. Moreover, it is significant to note that Ia reacted more readily with the carbonyl reagents than did Ib. In fact, the aryl-silicon bond of Ia appears to be the most reactive C-Si bond thus far encountered in our study of the cleavage of silylaromatic systems. It is also interesting that the general reactivity of Ib closely parallels that of the previously investigated 2-trimethylsilylbenzothiazole (5).

We are continuing our investigation of the cleavage of aryl-silicon bonds by neutral reagents to include additional silylaromatics and cleavage reagents.

## EXPERIMENTAL

The nmr spectra reported herein were obtained on a Varian A-60D spectrometer in carbon tetrachloride at concentrations of approximately 50% by volume and in reference to TMS as internal standard except as otherwise noted. The ir spectra reported were

TABLE I

## 2-Substituted 1-Methylimidazoles:

Compound	Substituent	B.p.(m.p.)°C	Analysis		
			C	H	N
Ia	-SiMe <sub>3</sub>	124°/45 mm	Found: 54.81 Calcd.: 54.48	8.88 9.16	
IIa	-CH(OSiMe <sub>3</sub> )Ph	86°/0.025 mm	Found: 64.42 Calcd.: 64.56	7.55 7.76	
IVa	-COPh	110°/0.15 mm	Found: 71.00 Calcd.: 70.94	5.46 5.42	14.77 15.05
VIa	-CO(C <sub>6</sub> H <sub>4</sub> -o-COOH)	(198-200°)	Found: 62.69 Calcd.: 62.60	4.10 4.39	12.21 12.17
VIIa	-CON(SiMe <sub>3</sub> )Ph	103°/0.05 mm	Found: 61.40 Calcd.: 61.49	6.92 7.02	
VIIIa	-CONHPh	(104-106°)	Found: 65.76 Calcd.: 65.64	5.64 5.52	20.93 20.88

## 2-Substituted 1-Methylbenzimidazoles:

Ib	-SiMe <sub>3</sub>	93°/0.05 mm	Found: 64.70 Calcd.: 64.64	7.68 7.91	13.49 13.71
IIb	-CH(OSiMe <sub>3</sub> )Ph	( 78- 80°)	Found: 69.82 Calcd.: 69.62	7.30 7.16	
Vb	-COOEt	110°/0.05 mm	Found: 64.55 Calcd.: 64.68	5.92 5.93	
VIb	-CO(C <sub>6</sub> H <sub>4</sub> -o-COOH)	(193°)	Found: 68.72 Calcd.: 68.56	4.10 4.32	
VIIb	-CON(SiMe <sub>3</sub> )Ph	155°/0.05 mm	Found: 66.46 Calcd.: 66.82	6.31 6.56	
VIIIb	-CONHPh	(160-162°)	Found: 71.66 Calcd.: 71.68	5.35 5.22	

obtained on a Perkin-Elmer 257 grating spectrophotometer utilizing potassium bromide pellets. All reactions were run under an anhydrous nitrogen atmosphere.

## 2-Trimethylsilyl-1-methylimidazole (Ia).

The dropwise addition of *n*-butyllithium (105 ml., 2.37 *M*) into a slurry of 1-methylimidazole (16.4 g., 0.2 mole) in 250 ml. of anhydrous ether at -70° afforded after stirring for 4 hours, 2-lithio-1-methylimidazole (6). Trimethylchlorosilane (27 g., 0.25 mole) was then added dropwise to this lithium derivative maintained at -70°, and the resultant mixture was allowed to warm to room temperature and was stirred for an additional 4 hours. The lithium chloride was filtered, the solution was concentrated *in vacuo* and the residue was fractionally distilled to afford 10 g. (33%) of Ia, b.p. 124°/45 mm,  $n_D^{25}$  1.4848.

*Anal.* Calcd. for C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>Si: C, 54.48; H, 9.16. Found: C, 54.81; H, 8.88.

## Nmr of Ia

(a) Position (δ) -	6.88	3.67	0.31
(b) Shape -	dbl.	sing.	sing.
(c) Integ. Ratio -	2	3	9
(d) Assignment -	arom.	N-Me	SiMe <sub>3</sub>

## Phenyl-2-(1-methyl)imidazolymethyl Trimethylsilyl Ether (IIa).

Benzaldehyde (8.3 g., 0.078 mole) was added dropwise with stirring to Ia (12 g., 0.078 mole). After the initial reaction had subsided, the reaction mixture was heated to 100° for 2 hours to insure complete reaction and was then fractionally distilled to afford 18.5 g. (91%) of IIa, b.p. 86°/0.025 mm,  $n_D^{25}$  1.5144.

*Anal.* Calcd. for C<sub>14</sub>H<sub>20</sub>N<sub>2</sub>OSi: C, 64.56; H, 7.76. Found: C, 64.42; H, 7.55.

Compound IIa upon heating with 95% ethanol containing a catalytic trace of dilute hydrochloric acid provided for quantitative conversion to phenyl-2-(1-methyl)imidazolymethanol (IIIa), m.p. 111-112.5° from acetone, lit. (8), m.p. 113°.

## Phenyl 2-(1-Methyl)imidazolyl Ketone (IVa).

Benzoyl chloride (7.7 g., 0.055 mole) was added dropwise with stirring to Ia (8.5 g., 0.055 mole). After the initial reaction had subsided, the reaction mixture was heated to 100° for 2 hours during which time the trimethylchlorosilane produced during the reaction was collected *via* normal distillation techniques. After cooling, the resultant product was washed with a bicarbonate water solution, extracted into chloroform, dried over anhydrous magnesium sulfate, concentrated *in vacuo* and fractionally distilled

## Nmr of IIa

(a) Position ( $\delta$ ) -	7.35-7.15	6.78	6.64	6.08	3.25	0.10
(b) Shape -	br. sing.	spl. sing.	spl. sing.	sing.	sing.	sing.
(c) Integ. Ratio -	5	1	1	1	3	9
(d) Assignment -	phenyl	imidyl.	imidyl.	C-H	N-Me	SiMe <sub>3</sub>

to afford 8.5 g. (84%) of IVa, b.p. 110°/0.15 mm,  $n_D^{25}$  1.6200.  
*Anal.* Calcd. for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O: C, 70.94; H, 5.42; N, 15.05.  
 Found: C, 71.00; H, 5.46; N, 14.77.

## Nmr of IVa

(a) Position ( $\delta$ ) -	8.5-8.3	7.55-7.25	7.02	6.9	3.82
(b) Shape -	mlt.	mlt.	sing.	sing.	sing.
(c) Integ. Ratio -	2	3	1	1	3
(d) Assignment -	phenyl	phenyl	imidyl.	imidyl.	N-Me

## Ethyl 2-(1-Methyl)imidazolecarboxylate (Va).

Ethyl chloroformate (5.65 g., 0.052 mole) was added dropwise with stirring to Ia (8 g., 0.052 mole). After the initial reaction had subsided, the reaction mixture was heated to 100° for 2 hours during which time the trimethylchlorosilane produced was collected. The resultant product was washed with a bicarbonate water solution, extracted with chloroform, dried over anhydrous magnesium sulfate, concentrated *in vacuo* and fractionally distilled to afford 7.1 g. (89%) of Va, b.p. 120°/2.5 mm,  $n_D^{25}$  1.5080, m.p. 44-46°, lit. (6), b.p. 55°/0.3 mm.

## 2-Carboxyphenyl 2-(1-Methyl)imidazolyl Ketone (VIa).

Phthalic anhydride (9.6 g., 0.065 mole) and Ia (10 g., 0.065 mole) were mixed and gently heated to 45°, at which temperature an exothermic reaction was observed. The reaction mixture was further heated to 100° for 2 hours. After exposure to the atmosphere, the thick black liquid product provided a solid which was recrystallized from ethanol to afford 12.8 g. (86%) of VIa, m.p. 198-200° dec.

*Anal.* Calcd. for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>: C, 62.60; H, 4.39; N, 12.17.  
 Found: C, 62.69; H, 4.10; N, 12.21.

## Nmr of VIa

(solvent, DMSO; int. std., DMSO at 2.62  $\delta$ )

(a) Position ( $\delta$ ) -	8.2-7.6	7.54	7.15	4.14
(b) Shape	mlt.	sing.	sing.	sing.
(c) Integ. Ratio -	4	1	1	3
(d) Assignment	phenyl	imidyl.	imidyl.	N-Me

The ir spectrum of VIa exhibited no acid upon proton stretch from 2.6-3.2  $\mu$  but did exhibit medium to strong bands from 3.7-4.3  $\mu$  indicative of the salt formation between the imidazolyl nitrogen and the carboxylic acid proton.

*N*-Trimethylsilyl-*N*-phenyl-2-(1-methyl)imidazolecarboxamide (VIIa).

Phenyl isocyanate (6.95 g., 0.0585 mole) was added dropwise with stirring to Ia (9 g., 0.0585 mole). After the initial reaction

had subsided, the reaction mixture was heated to 100° for 2 hours and then fractionally distilled to afford 15.1 g. (95%) of VIIa, b.p. 103°/0.05 mm,  $n_D^{25}$  1.5604.

*Anal.* Calcd. for C<sub>14</sub>H<sub>19</sub>N<sub>3</sub>OSi: C, 61.49; H, 7.02. Found: C, 61.40; H, 6.92.

## Nmr of VIIa

(a) Position ( $\delta$ ) -	7.4-6.9	6.75	3.87	0.19
(b) Shape -	mlt.	sing.	sing.	sing.
(c) Integ. Ratio -	6	1	3	9
(d) Assignment -	arom.	imidyl.	N-Me	SiMe <sub>3</sub>

Upon exposure to the atmosphere, VIIIa was quantitatively converted to *N*-phenyl-2-(1-methyl)imidazolecarboxamide (VIIIa), m.p. 104-106° from benzene-hexane.

*Anal.* Calcd. for C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O: C, 65.64; H, 5.52; N, 20.88.  
 Found: C, 65.76; H, 5.64; N, 20.93.

## Nmr of VIIIa

(solvent, acetone; int. std, acetone at 2.17  $\delta$ )

(a) Position ( $\delta$ ) -	9.80	8.1-7.0	4.13
(b) Shape -	sing.	mlt.	sing.
(c) Integ. Ratio -	1	7	3
(d) Assignment -	N-H	arom.	N-Me

## 1-Methylbenzimidazole (IX).

The reaction of benzimidazole (23.6 g., 0.2 mole) and iodo-methane (28.4 g., 0.2 mole) in an alcoholic-potassium hydroxide solution, according to the procedure of Pozharskii, *et al.* (10), afforded after fractional distillation 18.5 g. (70%) of IX, b.p. 96°/0.15 mm,  $n_D^{25}$  1.6015, m.p. 60-61.5° from benzene-hexane, lit. (7) b.p. 99-102°/0.5 mm, m.p. 60-61°.

## 2-Trimethylsilyl-1-methylbenzimidazole (Ib).

The dropwise addition of *n*-butyllithium (54.5 ml., 2.37 *M*) into a slurry of IX (13.2 g., 0.1 mole) in 300 ml. of anhydrous ether at -70° afforded, after stirring for 2 hours at -70°, 2-lithio-1-methylbenzimidazole (7). Trimethylchlorosilane (14 g., 0.13 mole) was then added dropwise to this ethereal solution at -70° and the mixture was allowed to warm to room temperature and was stirred for an additional 4 hours. The lithium chloride was filtered, the solution was concentrated *in vacuo* and the residue was fractionally distilled to afford 16.1 g. (79%) of Ib, b.p. 93°/0.05 mm,  $n_D^{25}$  1.5629. Compound Ib was further purified for elemental analysis by preparative glc with an Aerograph Autoprep Model A-700 gas chromatograph using a 20 ft. by 3/8 in. column packed with 30% SE-30 on Chrom W. A column temperature of 300° and a helium flow rate of 35 ml./min. was employed to afford a sample of Ib,  $n_D^{25}$  1.5560.

*Anal.* Calcd. for  $C_{11}H_{16}N_2Si$ : C, 64.64; H, 7.91; N, 13.71. Found: C, 64.70; H, 7.68; N, 13.49.

	Nmr of Ib			
(a) Position ( $\delta$ ) -	7.8-7.0	3.59	0.38	
(b) Shape -	mlt.	sing.	sing.	
(c) Integ. Ratio -	4	3	9	
(d) Assignment -	arom.	N-Me	SiMe <sub>3</sub>	

Phenyl-2-(1-methyl)benzimidazolymethyl Trimethylsilyl Ether (IIb).

Benzaldehyde (4.15 g., 0.0392 mole) and Ib (8 g., 0.0392 mole) were allowed to react at 180° for 16 hours to afford after an initial fractional distillation and subsequent recrystallizations from hexane 10.5 g. (86%) of IIb, b.p. 130°/0.05 mm,  $n_D^{25}$  1.5737, m.p. 78-80°.

*Anal.* Calcd. for  $C_{18}H_{22}N_2OSi$ : C, 69.62; H, 7.16. Found: C, 69.82; H, 7.30.

	Nmr of IIb			
(a) Position ( $\delta$ ) -	7.8-7.0	6.3	3.43	0.10
(b) Shape -	mlt.	sing.	sing.	sing.
(c) Integ. Ratio -	9	1	3	9
(d) Assignment -	arom.	C-H	N-Me	SiMe <sub>3</sub>

Compound IIb upon heating with 95% ethanol containing a catalytic trace of dilute hydrochloric acid provided for quantitative conversion to phenyl-2-(1-methyl)benzimidazolymethanol (IIIb), m.p. 159-161°, lit. (11), m.p. 158-160°.

Phenyl 2-(1-Methyl)benzimidazolyl Ketone (IVb).

Benzoyl chloride (4.8 g., 0.0342 mole) and Ib (7 g., 0.0342 mole) were heated with stirring at 100° for 3 hours during which time the trimethylchlorosilane produced was collected. The reaction mixture was then washed with a sodium bicarbonate water solution, the water decanted and the resultant product recrystallized from heptane to yield 6.5 g. (80%) of IVb, m.p. 68-70°, lit. (12), m.p. 69-71°.

Ethyl 2-(1-Methyl)benzimidazolecarboxylate (Vb).

Ethyl chloroformate (5.3 g., 0.049 mole) was added dropwise with stirring to Ib (10 g., 0.049 mole). After the initial reaction had subsided, the reaction mixture was heated to 100° for 2 hours during which time the trimethylchlorosilane produced was collected. The resultant product was washed with a sodium bicarbonate water solution, extracted into chloroform, dried over anhydrous magnesium sulfate, concentrated *in vacuo* and fractionally distilled to afford 7.2 g. (72%) of Vb, b.p. 110°/0.05 mm,  $n_D^{25}$  1.5805.

*Anal.* Calcd. for  $C_{11}H_{12}N_2O_2$ : C, 64.68; H, 5.93. Found: C, 64.55; H, 5.92.

	Nmr of Vb			
(a) Position ( $\delta$ ) -	7.9-7.1	4.35	3.91	1.40
(b) Shape -	mlt.	qrt.	sing.	trp.
(c) Integ. Ratio -	4	2	3	3
(d) Assignment -	arom.	CH <sub>2</sub>	N-Me	CH <sub>3</sub>

2-Carboxyphenyl 2-(1-Methyl)benzimidazolyl Ketone (VIb).

The reaction of phthalic anhydride (5.8 g., 0.0391 mole) and Ib (8 g., 0.0391 mole) at 120° for 2 hours afforded, after exposure of the product to the atmosphere and recrystallization from ethanol, 7.75 g. (71%) of VIb, m.p. 193° dec.

*Anal.* Calcd. for  $C_{16}H_{12}N_2O_3$ : C, 68.56; H, 4.32. Found: C, 68.72; H, 4.10.

	Nmr of VIb		
	(solvent, DMSO; int. std., DMSO at 2.62 $\delta$ )		
(a) Position ( $\delta$ ) -	8.2-7.3	4.27	
(b) Shape -	mlt.	sing.	
(c) Integ. Ratio -	8	3	
(d) Assignment -	arom.	N-Me	

The ir spectrum of VIb exhibited no acid proton stretch from 2.6-3.2  $\mu$  but did exhibit medium to strong bands from 3.7-4.2  $\mu$  indicative of the salt formation between the benzimidazolyl nitrogen and the carboxylic acid proton.

*N*-Trimethylsilyl-*N*-phenyl-2-(1-methyl)benzimidazolecarboxamide (VIIb).

Phenyl isocyanate (5.25 g., 0.044 mole) was added dropwise with stirring to Ib (9 g., 0.044 mole). After the initial reaction had subsided, the reaction mixture was heated to 100° for 2 hours and subsequently fractionally distilled to afford 12.5 g. (88%) of VIIb, b.p. 155°/0.05 mm,  $n_D^{25}$  1.6031.

*Anal.* Calcd. for  $C_{18}H_{21}N_3OSi$ : C, 66.82; H, 6.56. Found: C, 66.46; H, 6.31.

	Nmr of VIIb		
(a) Position ( $\delta$ ) -	7.9-7.0	3.98	0.28
(b) Shape -	mlt.	sing.	sing.
(c) Integ. Ratio -	3 (9)	1 (3)	3 (9)
(d) Assignment -	arom.	N-Me	SiMe <sub>3</sub>

Upon exposure to the atmosphere, VIIb was quantitatively converted to *N*-phenyl-2-(1-methyl)benzimidazolecarboxamide (VIIIb), m.p. 160-162° from benzene-hexane.

*Anal.* Calcd. for  $C_{15}H_{13}N_3O$ : C, 71.68; H, 5.22. Found: C, 71.66; H, 5.35.

	Nmr of VIIIb		
	(solvent, DMSO; int. std., DMSO at 2.62 $\delta$ )		
(a) Position ( $\delta$ ) -	10.87	8.2-7.2	4.25
(b) Shape -	sing.	mlt.	sing.
(c) Integ. Ratio -	1	9	3
(d) Assignment -	N-H	arom.	N-Me

Acknowledgment.

We gratefully acknowledge support of this investigation by the Paint Research Institute. We also thank Dr. W. H. Daudt of Dow-Corning Corporation for supplying us with generous quantities of silicon reagents.

## REFERENCES

- (1) To whom inquiries should be directed.
- (2) D. G. Anderson, M. A. M. Bradney and D. E. Webster, *J. Chem. Soc. B*, 450 (1968).
- (3) F. H. Pinkerton and S. F. Thames, *J. Heterocyclic Chem.*, 6, 433 (1969).
- (4) F. H. Pinkerton and S. F. Thames, *J. Organometallic Chem.*, 24, 623 (1970).
- (5) F. H. Pinkerton and S. F. Thames, *J. Heterocyclic Chem.*, 8, 257 (1971).
- (6) D. A. Shirley and P. W. Alley, *J. Am. Chem. Soc.*, 79, 4922 (1957).
- (7) P. W. Alley and D. A. Shirley, *J. Org. Chem.*, 23, 1791 (1958).
- (8) A. M. Roe, *J. Chem. Soc.*, 2195 (1963).
- (9) J. R. Pratt, F. H. Pinkerton and S. F. Thames, *J. Organometallic Chem.*, in press.
- (10) A. F. Pozharskii and A. M. Simonov, *Zh. Obshch. Khim.*, 33, 179 (1963); *Chem. Abstr.*, 59, 601a (1963).
- (11) A. F. Wagner, P. E. Wittreich, A. Lusi and K. Folkers, *J. Org. Chem.*, 27, 3236 (1962).
- (12) S. C. Agarwal and T. R. Seshadri, *Tetrahedron*, 20, 17 (1964).